Roughness-induced energetic disorder at the metal/organic interface

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The amplitude of the roughness-induced energetic disorder at the metal/organic interface was calculated. It was found that for moderately rough electrodes, the correction to the electrostatic image potential at the charge location is small. As a result, roughness-induced energetic disorder does not noticeably affect charge carrier injection.

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Effective injection of charge carriers is a major requirement for efficient and reliable performance of electronic organic devices (light-emitting diodes, thin-film transistors, and others).[1] Understanding charge injection is intimately connected to the structure of the metal/organic interface (or the interface of an organic material with another conductive material, such as indium tin oxide), and the detailed knowledge of this structure is important for other processes and applications. Recent experimental studies indicate that the Richardson-Schottky thermionic injection

$$j \propto \exp\left(-\frac{e\phi}{kT} + \gamma\sqrt{E}\right) \tag{1}$$

is a good starting point for the description of injection process in organic devices.[1–3] Here, j is the injected current density, ϕ is the height of the barrier at the interface, and E is an applied electric field. At the same time, measurements at low temperature show that the decrease of the injection current density is much smaller than the anticipated decrease according to the Richardson-Schottky model.[4,5] It was suggested that the reason for this discrepancy is the effect of energetic disorder in the organic material.[2] Usually, the calculation of the effect of disorder on injection is carried out using disorder parameters estimated from the charge transport data;[4,5] this means that these parameters describe the disorder in the bulk of the organic material. The experimental data clearly indicate, though, that in some cases, a surface dipolar layer is formed at the metal/organic interface.[6,7] It is very reasonable to assume that this layer has some degree of disorder and, hence, will provide an additional contribution to the energetic disorder at the interface.[8,9]

Recently, roughness at the metal/organic interface was suggested as the source of additional energetic disorder, localized near the interface.[9] A calculation of the standard deviation of the disorder $\sigma(z_0)$ for a point charge e located at distance z_0 from the mean plane of the weakly rough metal surface having profile $h(x,y)$ may be carried out in the following way (we assume that the mean plane of the electrode is located at $z=0$). Let us suppose that $z_0 \ll l$, where l is the surface correlation length. We can then consider the electrode surface at the vicinity of a charge as a flat plane and treat surface deviation $h(x,y)$ from the mean plane as a constant. The change of the image potential at the charge location due to the shift of the surface position by h is (in the first order in h)

$$\delta\varphi(z_0) \approx -\frac{eh}{2\varepsilon z_0^2} \tag{2}$$

and $\sigma(z_0)$ is estimated as

$$\sigma^2(z_0) = e^2\langle[\delta\varphi(z_0)]^2\rangle = \frac{e^4 h_0^2}{4\varepsilon^2 z_0^4}, \tag{3}$$

where the angular brackets denote an average over the ensemble of realizations of the surface roughness, $h_0^2 = \langle h^2(x,y)\rangle$ is the roughness variance, and ε is a dielectric constant. The mean plane of the electrode is defined in such a way that $\langle h(x,y)\rangle = 0$. Equation (3) is exactly the result of Ref. 9, though obtained in a much simpler way.

The important parameter for charge injection is the energetic disorder directly at the interface; i.e., in first several layers of organic transport molecules adjacent to the electrode. If for the very first layer $z_0 = 6$ Å, $h_0 = 3.5$ Å, and $\varepsilon = 1$, then $\sigma(z_0) = 0.7$ eV (Ref. 9). Yet the validity of Eq. (3) for short distances is very dubious because of the basic assumption that organic molecules in any particular layer of organic material are situated at a *constant distance* z_0 *from the mean plane of the electrode*[9] [see Fig. 1(a)]. The size of a typical transport molecule (8–10 Å) is small in comparison to the surface correlation length (typically, $l = 20$–50 nm, Ref. 10). In this situation it is natural to expect that a better model of the interface is one wherein the molecules follow the electrode profile, and any particular layer is located at the *constant distance* z_0 *to the actual surface of the electrode* [Fig. 1(b)].

Indeed, the model of Ref. 9 demonstrates two unrealistic features. First, for a reasonable surface correlation length $l \geqslant 15$–20 nm and a rms roughness $h_0 = 3$–10 Å, it predicts empty voids between the surface of the electrode and the first organic layer with a depth up to 1 nm or greater, and a size across the surface comparable to l. These voids are situated in the regions where the valleys of the surface profile are located. Such large voids are not consistent with microscopy

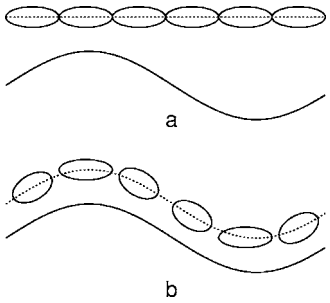

FIG. 1. Two models of the arrangement of organic molecules (ellipsoids) at the rough surface of the electrode (solid line). (a) The first layer is located at constant distance to the mean electrode plane (Ref. 9). (b) Molecules in the first layer are located at a constant distance to the surface of the electrode.

pictures at metal/organic interfaces, which show the organic to conform to the surface features of the metal.[11] Second, if $h_0=3.5$ Å and $z_0=6$ Å for the first layer of organic molecules, then a lot of hills of the electrode profile should literally overlap with the organic material (deviations of the surface profile from the mean plane equal to 2–3 h_0 are not very unusual). This behavior is unphysical.

We are going to demonstrate that in our new model [Fig. 1(b)], $\sigma(z_0)$ differs drastically from the estimation in Eq. (3). The calculation of $\sigma(z_0)$ along the profile of the rough metal surface is the major difference between our paper and the paper of Rahman and Maradudin,[12] in which the general expression for the mean image potential for a rough dielectric interface was obtained. In this paper we use a different technique, which is better suited for explicit calculation of roughness-induced disorder. Additionally, since we aim to understand the role of roughness in the formation of the energetic disorder at the interface, we neglect the contribution arising from the variation of the chemical composition of the electrode and the transport layer across the electrode surface.

The potential for a point charge located at the vicinity of a rough metal surface obeys the Poisson equation

$$\Delta\varphi = -\frac{4\pi e}{\varepsilon}\delta(\vec{r}-\vec{r}_0) \tag{4}$$

with the boundary condition

$$\varphi|_{z=h(x,y)} = 0. \tag{5}$$

We assume that the roughness is small $h_0/l \ll 1$, and Eq. (4) can be treated via a perturbation theory approach. We are going to calculate the leading contribution only. A possible approach to perform this calculation is to transform to coordinates $z_{\text{new}}=z-h(x,y)$, so that for new z the boundary condition is set for $z=0$. In the new coordinates, the Poisson equation takes the form

$$\Delta_\perp\varphi + \frac{\partial^2\varphi}{\partial z^2}\left[\left(\frac{\partial h}{\partial x}\right)^2 + \left(\frac{\partial h}{\partial y}\right)^2 + 1\right] - 2\left(\frac{\partial^2\varphi}{\partial x\partial z}\frac{\partial h}{\partial x} + \frac{\partial^2\varphi}{\partial y\partial z}\frac{\partial h}{\partial y}\right) - \frac{\partial\varphi}{\partial z}\Delta_\perp h = -\frac{4\pi e}{\varepsilon}\delta(\vec{r}-\vec{z}_0), \tag{6}$$

where $\Delta_\perp$ is a two-dimensional (2D) Laplacian and we assume $\vec{z}_0=(0,0,z_0)$. Note that in the new coordinates, the condition $z_0=$const is approximately equivalent to a constant distance to the profile of the electrode (with a small correction proportional to h_0^2/l^2 and insignificant to our analysis).

Let us try to find a formal solution as a series

$$\varphi = \sum_{n=0}^{\infty}\varphi_n, \quad \varphi_n \sim O(h^n), \quad \varphi_n|_{z=0} = 0,$$

$$\varphi_0(\vec{r}) = \frac{e}{\varepsilon|\vec{r}-\vec{z}_0|} - \frac{e}{\varepsilon|\vec{r}+\vec{z}_0|}. \tag{7}$$

The first-order correction is

$$\varphi_1(\vec{r}) = \int d\vec{r}_1 G(\vec{r},\vec{r}_1)J(\vec{r}_1). \tag{8}$$

Here, $G(\vec{r},\vec{r}_1)$ is the Green function for the Laplace operator with zero boundary condition at $z=0$, while the source term is

$$J(\vec{r}) = 2\left(\frac{\partial^2\varphi_0}{\partial x\partial z}\frac{\partial h}{\partial x} + \frac{\partial^2\varphi_0}{\partial y\partial z}\frac{\partial h}{\partial y}\right) + \frac{\partial\varphi_0}{\partial z}\Delta_\perp h = -\frac{e}{\varepsilon}\frac{\partial}{\partial z_0}\left[2\left(\frac{\partial P}{\partial x}\frac{\partial h}{\partial x} + \frac{\partial P}{\partial y}\frac{\partial h}{\partial y}\right) + P\Delta_\perp h\right],$$

$$P(\vec{r}) = \frac{1}{|\vec{r}-\vec{z}_0|} + \frac{1}{|\vec{r}+\vec{z}_0|}. \tag{9}$$

Note that, in our case, the correction to φ_0 depends not on $h(x,y)$ itself, but on its derivatives, and vanishes for $h(x,y)=$const, as it should be.

The Green function has the form[13]

$$G(\vec{r},\vec{r}_1) = \frac{1}{4\pi^2}\int d\vec{k}e^{-i\vec{k}(\vec{\rho}-\vec{\rho}_1)}G_k(z,z_1), \tag{10}$$

where $\vec{k}$ and $\vec{\rho}=(x,y)$ are 2D vectors, and the Green function $G_k(z,z_1)$ obeys the equation

$$\frac{d^2G_k}{dz^2} - k^2G_k = \delta(z-z_1), \quad G_k(0,z_1) = 0. \tag{11}$$

The solution of Eq. (11) is

$$G_k(z,z_1) = -\frac{1}{k}\sinh kz_- \exp(-kz_+),$$

$$z_+ = \max(z,z_1), \quad z_- = \min(z,z_1). \tag{12}$$

We are going to calculate the correction (8) for $\vec{r}=\vec{z}_0$ only, because $\sigma^2(z_0)=e^2\langle\varphi_1^2(\vec{z}_0)\rangle$. A simple but lengthy calculation gives for φ_1

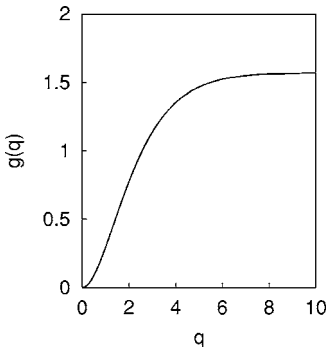

FIG. 2. Function $g(q)$.

$$\varphi_1(\vec{z}_0) = \frac{e}{4\pi^3\varepsilon}\int d\vec{k}_1 d\vec{k}_2 h_{\vec{k}_1-\vec{k}_2}\exp[-(k_1+k_2)z_0] \times[\cosh(k_1-k_2)z_0 - 1], \quad (13)$$

and $h_{\vec{k}}$ is a Fourier transform of $h(\vec{\rho})$. The integral (13) can be simplified further. Let us make a transition to new vector coordinates $\vec{p}=(\vec{k}_1+\vec{k}_2)/2$, $\vec{q}=\vec{k}_1-\vec{k}_2$. Then,

$$\varphi_1(\vec{z}_0) = \frac{e}{4\pi^3\varepsilon z_0^2}\int d\vec{q} g(qz_0) h_{\vec{q}}, \quad (14)$$

where

$$g(q) = \int d\vec{p}\exp(-R)(\cosh Q - 1),$$

$$R = \left|\vec{p}+\tfrac{1}{2}\vec{q}\right| + \left|\vec{p}-\tfrac{1}{2}\vec{q}\right|, \quad Q = \left|\vec{p}+\tfrac{1}{2}\vec{q}\right| - \left|\vec{p}-\tfrac{1}{2}\vec{q}\right|. \quad (15)$$

Function $g(q)$ can be easily estimated for $q \ll 1$ and $q \gg 1$. In the first case we can expand the hyperbolic cosine in the integral (15) in power series of $\vec{q}$, thus obtaining

$$g(q) \approx \int d\vec{p}\left(\frac{\vec{p}\cdot\vec{q}}{p}\right)^2 \exp(-2p) = \frac{\pi q^2}{8}. \quad (16)$$

In the opposite case ($q \gg 1$), analysis shows that the only significant (and equal) contributions to Eq. (15) goes from $\vec{p} \approx \pm\frac{1}{2}\vec{q}$, so setting $\vec{p}=\frac{1}{2}\vec{q}+\vec{s}$, we have

$$g(q) \approx \int d\vec{s}\exp(-2s) = \frac{\pi}{2}. \quad (17)$$

The general behavior of $g(q)$ is shown in Fig. 2.

Finally, the variance of roughness-induced energetic disorder is

$$\sigma^2(z_0) = e^2\langle\varphi_1^2(z_0)\rangle = \frac{e^4 h_0^2}{4\pi^4\varepsilon^2 z_0^4}\int d\vec{q} g^2(qz_0) C_{\vec{q}}. \quad (18)$$

This equation is the major result of this paper. Here, $C_{\vec{q}}$ is the Fourier transform of the surface correlation function, which we define in a usual way (assuming spatially homogeneous roughness):

$$\langle h(\vec{\rho})h(\vec{\rho}_1)\rangle = h_0^2 C(\vec{\rho}-\vec{\rho}_1) \quad (19)$$

with $C(0)=1$, so that $\langle h^2(\vec{\rho})\rangle = h_0^2$. For homogeneous roughness,

$$\langle h_{\vec{k}} h_{\vec{k}_1}\rangle = 4\pi^2 h_0^2 C_{\vec{k}}\delta(\vec{k}+\vec{k}_1). \quad (20)$$

If $z_0 \gg l$, we can then replace $g(qz_0)$ by its limit value of $\pi/2$, and in this case

$$\sigma^2(z_0) \approx \frac{e^4 h_0^2}{4\varepsilon^2 z_0^4}. \quad (21)$$

This result is equivalent to Eq. (3), but it is valid only far away from the rough electrode surface. The reason for the equivalence of Eq. (21) and Eq. (3) is the need to cancel the leading term in Eq. (14) in the old (physical) coordinate system. Indeed, as it follows from Eq. (14) for $z_0 \gg l$,

$$\varphi_1(z_0) = \frac{eh}{2\varepsilon z_0^2} + o\left(\frac{1}{z_0^2}\right)\Omega[h], \quad (22)$$

where Ω is some integral operator. Image potential at the charge location is

$$-\frac{e}{2\varepsilon z_0} + \frac{eh}{2\varepsilon z_0^2} + o\left(\frac{1}{z_0^2}\right)\Omega[h] = -\frac{e}{2\varepsilon z_0^{\text{old}}} + o\left(\frac{1}{(z_0^{\text{old}})^2}\right)\Omega[h] + O(h^2) \quad (23)$$

(here z_0^{old} denotes the distance to the mean plane of the electrode). This result means that in the old (physical) coordinate system the correction to the image potential in the first order in h decays faster than $1/(z_0^{\text{old}})^2$ for large distances. This is not surprising because this kind of decay is possible only for $h \approx \text{const}$, which is not the case for $z_0 \gg l$, where many uncorrelated domains of the rough surface contribute to the image potential.

All these intricacies are not important for charge injection, where a relevant distance to the surface of the electrode is small. If $z_0 \ll l$, then

$$\sigma^2(z_0) \approx \frac{e^4 h_0^2}{256\pi^2\varepsilon^2}\int d\vec{q} q^4 C_{\vec{q}} \propto \frac{e^4 h_0^2}{\varepsilon^2 l^4}. \quad (24)$$

The latter estimation is valid if $C(\vec{\rho})$ can be characterized by the scale l only, and the integral in Eq. (24) converges for $q \to \infty$. If we assume a Gaussian correlation function

$$C(\vec{\rho}) = \exp\left(-\frac{\rho^2}{2l^2}\right), \quad (25)$$

which is a good approximation for indium tin oxide electrodes,[10] then for $z_0 \ll l$,

$$\sigma^2(z_0) \approx \frac{e^4 h_0^2}{8\varepsilon^2 l^4}. \quad (26)$$

Eq. (26) is similar to Eq. (3) with the only crucial difference: z_0 is replaced by l. For the roughest electrode, mentioned in Ref. 10, with $h_0=4$ nm and $l=14$ nm, we have at the interface $\sigma \approx 0.01$ eV. This means that the magnitude of the dis-

order at the interface is too small to provide a noticeable effect on injection. In addition, because the dependence of the standard deviation on distance is very different from Eq. (3), it cannot provide a reasonable explanation for the particular kind of current-voltage dependences reported in Ref. 9.

Let us consider the case when the integral (24) does not converge for $q \to \infty$. This is the case of the fractal rough surface with a correlation function

$$C_{\vec{k}} = \frac{Al^2}{(1+k^2l^2)^{1+\alpha}}, \quad A = 4\pi\alpha\left[1 - \frac{1}{(1+k_c^2l^2)^{\alpha}}\right]^{-1}, \quad (27)$$

here $0 \leqslant \alpha < 1$ (Ref. 14). In fact, any fractal surface can be realized as an intermediate asymptotic only, for some spatial scale range, thus the proper cutoff k_c is assumed in Eq. (27). For a clear physical reason (discrete nature of a real metal surface) $k_c \ll 1/a$ where a is a typical interatom distance, while $k_c l \gg 1$. This means that $z_0 k_c \lesssim 1$ for the organic layers closest to the metal surface. Hence, we can still use the small-q asymptotic of $g(q)$ and

$$\sigma^2(z_0) \approx \frac{Ae^4h_0^2l^2}{128\pi\varepsilon^2}\int_0^{k_c} dq \frac{q^5}{(1+q^2l^2)^{1+\alpha}} \approx \frac{Ae^4h_0^2(k_cl)^{2(2-\alpha)}}{256(2-\alpha)\pi\varepsilon^2l^4}. \quad (28)$$

In the most favorable for large σ case $\alpha \approx 0$,

$$\sigma(z_0) \approx \frac{\pi e^2 h_0 k_c^2}{8\varepsilon\sqrt{\ln(k_cl)}}, \quad (29)$$

and for $h_0 = 5$ Å the value of σ becomes comparable with the bulk value of 0.1 eV only for $k_c \gtrsim 0.1$ Å^{-1}. Such a value for k_c seems to be unreasonably large. Scanning microscopy data indicate that typically the Gaussian correlation function (25) is a good approximation for rough electrode surfaces at the nanometer scale.[10] Fractal surfaces have indeed been observed in clusters formed by small metal particles, but the relevant spatial scale was very different; even the size of the individual metal particle was no less than 10 nm (Refs. 15 and 16): in this case, $k_c < 0.01$ Å^{-1}.

In conclusion, we have found that the contribution from the roughness-induced energetic disorder in the near vicinity of the interface is typically too weak to provide a noticeable effect on injection. Therefore, the simplest model of a plane electrode surface provides a good starting approximation for charge injection in organic devices with moderately rough electrodes.

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[1] J. C. Scott, J. Vac. Sci. Technol. A **21**, 521 (2003).
[2] V. I. Arkhipov, E. V. Emelianova, Y. H. Tak, and H. Bässler, J. Appl. Phys. **84**, 848 (1998).
[3] J. C. Scott and G. G. Malliaras, Chem. Phys. Lett. **299**, 115 (1999).
[4] T. Van Woudenbergh, P. W. M. Blom, M. C. J. M. Vissenberg, and J. N. Huilberts, Appl. Phys. Lett. **79**, 1697 (2001).
[5] B. H. Hamadani and D. Natelson, J. Appl. Phys. **97**, 064508 (2005).
[6] H. Ishii, K. Sugiyama, E. Ito, and K. Seki, Adv. Mater. (Weinheim, Ger.) **11**, 605 (1999).
[7] D. Cahen and A. Kahn, Adv. Mater. (Weinheim, Ger.) **15**, 271 (2003).
[8] M. A. Baldo and S. R. Forrest, Phys. Rev. B **64**, 085201 (2001).
[9] B. N. Limketkai and M. A. Baldo, Phys. Rev. B **71**, 085207 (2005).
[10] S. V. Novikov, Macromol. Symp. **212**, 191 (2004).
[11] A. C. Dürr, F. Schreiber, M. Kelsch, H. D. Carstanjen, and H. Dosch, Adv. Mater. (Weinheim, Ger.) **14**, 961 (2002).
[12] T. S. Rahman and A. A. Maradudin, Phys. Rev. B **21**, 504 (1980).
[13] S. V. Novikov and A. V. Vannikov, Synth. Met. **121**, 1387 (2001).
[14] Y.-P. Zhao, G.-C. Wang, T.-M. Lu, G. Palasantzas, and J. T. M. De Hosson, Phys. Rev. B **60**, 9157 (1999).
[15] D. P. Tsai, J. Kovacs, Z. Wang, M. Moskovits, V. M. Shalaev, J. S. Suh, and R. Botet, Phys. Rev. Lett. **72**, 4149 (1994).
[16] M. C. Chen, S. D. Tsai, M. R. Chen, S. Y. Ou, W.-H. Li, and K. C. Lee, Phys. Rev. B **51**, 4507 (1995).